Strip Material Used for Shadow Mask Having Improved Post-Etching Shape

BACKGROUND OF INVENTION

1. Field of Invention

The present invention relates to a mild-steel strip or an Fe-Ni alloy strip used for a shadow mask having improved post-etching shape.

2. Description of Related Art

A strip for a shadow mask of a Braun tube is usually produced by rolling. The strip for the shadow mask is degreased and then subjected to application of photo-resist on both surfaces. A pattern of through holes is delineated on the photo-resist layer which is then developed. Ferric chloride solution is sprayed on both surfaces of the strip to form through holes. The strip is then cut into shadow-mask segments (c.f. Materia (Journal of Japan Institute for Metals), Vol. 36 (1977), No. 11, pages 1070-1074). The shadow-mask segments are conveyed by an automatic conveying line during the etching process or the manufacturing process of a Braun tube. The etched shadow masks should not be caught on the conveyer so as to avoid conveying failure. The flatness of the etched shadow mask is, therefore, important.

Residual stress of a strip for a shadow mask is schematically illustrated in Fig. 1. The direction across the major surfaces of a strip 1 is hereinafter referred to as the thickness direction. The direction of a strip 1 across the sides of a strip is hereinafter referred to as the width direction. The thickness of a strip 1 is denoted in Fig. 1 as "t". Figure. 1 illustrates that: the residual stress (σ) on the cross-sections, S_1 and S_2 parallel and perpendicular to the rolling direction (RD), respectively, distributes along the thickness direction. An example of actual measurement of residual stress (σ) is shown in Fig. 2.

As shown in Fig. 1, in a post-rolling strip for the shadow mask, the residual stress (σ) generated in the surface portions of a strip 1 as seen in the thickness direction is such that such portion is subjected to compression residual stress denoted as σ_c. Such compression residual stress (σ_c) is generated on both cross-sections, S_1 and S_2 parallel and perpendicular to the rolling directions(RD), respectively. Meanwhile, the residual stress (σ) generated in the central portion of a strip as seen in the thickness direction is such that such portion is subjected to tension denoted as σ_t. Such tensile residual stress (σ_t) is generated on both cross-sections, S_1 and S_2 parallel and perpendicular to the rolling direction (RD), respectively.

Through-holes of a shadow mask shown in Fig. 4 have on either side of the shadow mask an aperture in the form of a true circle having, for example, 130 μ m of diameter. This aperture is hereinafter referred to as the small aperture 2. The through-holes have on the other side an aperture in the form of a true circle and having, for example, 220 μ m of diameter. This aperture is hereinafter referred to as the large aperture 3. Figure. 4 also schematically illustrates how a shadow mask warps under the influence of the residual stress (σ). The apertures 2, 3 of a through-hole are non-symmetrical to and of different diameter from one another. This is because when the through holes are formed on a shadow mask, the etching amount of material in the side, where the large aperture 3 is formed, is greater than that on the other side, where the small aperture 2 is formed. The residual stress (σ) on both sides becomes therefore un-balanced, with the result that warp occurs.

The compressive stress (σ_c) in the surface portion, where the small apertures 2 are formed, can be treated as the internal stress of a compressed spring. On the other hand, the tensile stress in the central region can be treated as the internal stress of a extended spring. These springs exert mutual influence to balance the stresses. The warp occurs, therefore, after etching in such a manner that a convex shape is formed on a side of the small aperture 2.

Conventionally, the shadow masks for civilian use have only slightly non-symmetrical apertures, and slight warp generates under the influence of the residual stress. However, in a highly precise shadow mask, since the non-symmetry mentioned above is considerable, large warp occurs under the influence of the residual stress.

Generally speaking, the residual stress can be relieved by means of stress-relief annealing at a temperature lower than the recrystallization temperature. The warp after etching can thus be prevented. However, the stress-relief annealing increases the production cost. In addition, the stress-relief annealing does not greatly decrease the tensile strength (TS) but seriously decreases the 0.2% yield strength (YS). When the 0.2% YS becomes low, serious wrinkle is liable to occur in the subsequent etching process.

SUMMARY OF INVENTION

It is an object of the present invention to provide an Al-killed-steel rolled strip or an Fe-Ni based-alloy rolled strip produced by straightening, but not stress-relief annealing, enabling reduction of residual stress and the post-etching warp.

The present inventors discovered that the etching warp of an Al-killed steel rolled strip and an Fe-Ni alloy rolled strip can be suppressed by the straightening process

carried out after the final rolling under the following conditions (1) and (2) described below. As a result of elimination of the stress relief annealing, the production cost can be saved. In addition, the 0.2% YS of the same level as TS could be attained, that is, TS/0.2% YS $\leqq 1.03$.

(1) Residual stress distributes along the thickness direction on the cross sections S_1 and S_2 of a strip parallel and perpendicular to the rolling direction (RD), respectively, as described hereinabove. In other words, the cross sections S_1 and S_2 of a strip parallel and perpendicular to the rolling direction (RD), respectively, are subjected to the residual stress, which varies in the thickness direction. The maximum tensile residual stress (σ_t) generated on a central portion of the cross sections S_1 and S_2 mentioned above is adjusted to $50N/mm^2$ or less.

(2) A rectangle specimen 10(1) elongated in the rolling direction (RD) is sampled from a rolled strip 1 shown in Fig. 3 at a central portion as seen in the width direction. The long sides of a rectangle specimen 10(1) are 500 mm long, while the short sides of a rectangle specimen 10(1) are 50 mm wide. Another rectangle specimen 10(2) elongated in a direction perpendicular to the rolling direction (RD) is sampled from a rolled strip 1 shown in Fig. 3 at a central portion as seen in the width direction. The long sides of a rectangle specimen 10(2) are 500 mm long, while the short sides of a rectangle specimen 10(2) are 50 mm wide. As shown in the right-half of Fig. 3, the rectangle specimens 10(1) and 10(2) are clamped at one of the ends and are suspended downwards in the direction of the long sides thereof. Warp of the other non-clamped ends is measured. The rectangle specimen 10(1) warps in the rolling direction (RD). This warp is hereinafter referred to as the curl warp (Wc). The rectangle specimen 10(2) warps in a direction perpendicular to the rolling direction (RD) and this warp is hereinafter referred to as the gutter warp (Wg). The curl warp (Wc) and the gutter warp (Wg) are adjusted to 10 mm or less by means of straightening described hereinbelow.

BRIEF EXPLANATION OF DRAWINGS

Figure 1 is a schematic drawing illustrating the residual stress (σ) generated on the cross sections S_1 and S_2 of a strip parallel and perpendicular to the rolling direction (RD), respectively, and the residual stress (σ) distributed along the thickness direction.

Figure 2 is a graph showing an example of the distribution of residual stress along the thickness direction actually measured.

Figure 3 illustrates a method for sampling of rectangle specimens and measuring the warp.

Figure 4 schematically illustrates the mechanism of how warp occurs under the influence of the residual stress (σ).

Figure 5 schematically illustrates the warp of the shadow masks, which are etched and then separated from a strip.

Figure 6 illustrates a measuring method of warp by means of downward suspension.

Figure 7 is a schematic drawing of a straightening machine.

Figure 8 is a graph showing a straightening condition of the Fe – 36 mass % Ni alloy in an example.

DESCRIPTION OF PREERRED EMBODIMENTS

Al killed steel and Fe-Ni based alloy having from 34 to 38 mass % of the Ni content are generally used as the strip for a shadow mask. The Fe-Ni alloy exhibits a low coefficient of thermal expansion and is hence appropriate for a highly precise shadow mask. The elements other than the principal elements of these materials exert detrimental influence upon the coefficient of thermal expansion, the etching property, the formability and the like. Preferred elements other than the principal elements of Al-killed steel are: 0.010 mass % or less of C; 0.04 mass % or less of Si; 0.08 mass % or less of Al; from 0.10 to 0.60 mass % of Mn; 0.040 mass % or less of S; and, 0.035 mass % or less of P. The elements other than the principal elements of Fe-Ni alloy are preferably 0.10 mass % or less of C and 0.1 mass % or less of Si, and more preferably 0.05 mass % or less of Si; 0.05 mass % or less of Al; 0.5 mass % or less of Mn; 0.005 mass % or less S; and 0.005 mass % or less of P.

A high-strength Fe-Ni alloy, in which Ni is replaced with from 2 to 8 mass % of Co, is also provided for a shadow mask. That is, the Ni content is reduced to a range of from 30 to 35 mass %, and the Ni is replaced with from 2 to 8 mass % of Co. Co added in this range does not increase but rather decreases the coefficient of thermal expansion. In order to further strengthen the Fe-Ni alloy, Co and additionally, one or more of Nb, Ta, Hf, Ti and Zr are preferably added in an amount of from 0.05 to 0.8 mass %. When the total amount of Nb, Ta, Hf, Ti and Zr exceeds 0.8 mass %, the coefficient of thermal expansion seriously increases. The total amount of these elements is therefore limited to 0.8 mass % or less. In a case of adding these elements, the elements other than the principal elements of Fe-Ni alloy are preferably 0.10 mass % or less of C and 0.1 mass % or less of Si, and more preferably 0.05 mass % or less of Si; 0.05 mass % or less of Al; 0.5 mass % or less of Mn; 0.005 mass % or less S; and 0.005 mass % or less of P.

The residual stress (σ) on the cross-section S_1 parallel to the rolling direction

(RD) shown in Fig. 1 distributes in the thickness direction. Regardless of whether the residual stress (σ) is compressive or tensile, its principal direction is the rolling direction (RD). The residual stress (σ) on a cross-section S_2 perpendicular to the rolling direction (RD) shown in Fig. 1 distributes in the thickness direction. Regardless of whether residual stress (σ) is compressive or tensile, its principal direction is perpendicular to the rolling direction (RD). In a shadow mask according to the present invention, the tensile residual stress (σ_t) is present on a central portion of both sections S_1 and S_2. Such distribution of residual stress (σ) has been conventionally generated in a rolled but not stress-relief annealed strip. The highest tensile residual stress of more than 50N/mm^2 at a central portion causes large post-etching warp as is explained with reference to Fig. 4. Such residual stress is therefore limited to 50N/mm^2 or less according to the present invention.

Referring to Fig. 5, it is illustrated: how the etched shadow masks 6 are separated from a strip 1; and, the separated shadow masks 6 warp. One of the etched shadow masks 6(1) warps in the form of a curl, while the other etched shadow mask 6(2) warps in the form of a gutter. The residual stress distribution on the cross-sections S_1 and S_2 parallel and perpendicular to the rolling direction (RD), respectively, is the factor determining the direction of warp of a shadow mask.

It is known that in a strip rolled by bright rolls almost no residual stress generates on a cross-section S_2 (c.f. Fig. 1) perpendicular to the rolling direction (RD). A strip used for a shadow mask is finishing rolled by means of the special rolls described hereinafter. High residual stress, therefore, generates also on a cross-section S_2 perpendicular to the rolling direction (RD). The strips for a shadow mask are etched and stacked on one another to face the rolled surfaces with one another. The stacked strips are then heat-treated. In order to prevent adhesion of the strips during the heat treatment, the unevenness pattern referred to as the dull figure is copied from the surfaces of rolls, which have been shot blasted for example. When the rolling is carried out by means of rolls having large surface unevenness, the friction force on the surface of a strip is greater than in a case of rolling with bright rolls. The residual stress (σ) on a cross-section S_2 perpendicular to the rolling direction becomes, therefore, high. In a rolled strip, the residual stress (σ) on the cross-section S_1 in a direction parallel to the rolling direction (RD) is higher than the residual stress (σ) on the cross-section S_2 in a direction perpendicular to the rolling direction (RD). Straightening by means of levelers can decrease the residual stress (σ) on the cross section S_1 to a level equal to or less than the stress (σ) on a cross-section S_2 perpendicular to the rolling direction (RD). Therefore, the stress distribution on a cross-section S_2 parallel to the rolling direction

(RD) mainly determines the curl warp (Wc). while the stress distribution on a cross section S_2 perpendicular to the rolling direction (RD) mainly determines the gutter warp (Wg).

In order to attain small post-etching warp, the highest tensile residual stress(σ_t) in a central portion of the thickness direction must be 50N/mm^2 or less. Conditions of the leveler straightening for attaining low residual stress (σ) depend upon the condition of residual stress. Namely, when the rolling rolls have large surface unevenness, the friction force on the surface of a strip and hence the residual stress is large. The magnitude of residual stress is influenced by not only the surface roughness of the rolls but also the rolling conditions such as rolling speed, and viscosity of rolling oil. Factors, which influence the residual stress, are complicated. It is, therefore, difficult to precisely analyze the influencing factors. A shadow mask with low residual stress (σ) can be obtained by means of test straightening under various conditions and selecting narrow straightening conditions to reduce the residual strength.

Flatness of a post-etching shadow mask can be measured by placing the shadow mask on a horizontally placed flat platen in such a manner that the concave surface of the shadow mask is directed upward. The warp amount, i. e., the distance between the furthest bent side of a mask and the platen, is measured to determine the warp. This warp should be 2 mm or less. However, since the amount of absolute value of warp measured by this method is small, accurate warp may not be disadvantageously measured. The present inventors consequently conceived and arrived at an idea of the downward suspension method. That is, as shown in Fig. 6, one of the sides of the shadow mask 10 is fixed by means of a clamp 5 or the like on a flat sheet fixed perpendicularly. The other free side of the shadow mask 10 warps from the flat sheet 4. The distance between the other free side and the flat sheet 4 is measured to determine the warp. A shadow mask exhibiting 2 mm of warp according to the method of placing it on a flat platen exhibits 20 mm of warp according to the downward suspension method. It is, therefore, expected that the measurement accuracy is enhanced by as much as approximately 10 times.

It is presumed that the curl and gutter warps of the rectangle specimens sampled from a square sheet are 10 mm. This means that the residual stresses (σ) in different directions exist in the square sheet. Since the residual stresses (σ) are offset in the square sheet, when the square sheet is suspended for measuring the warp, almost no warp appears. Therefore, the rectangle specimens are used in the present invention to measure the warp of material before etching. In the rectangle specimens the offsetting effect is suppressed, and the warp can be precisely measured.

A strip used for a shadow mask having improved shape according to the present invention is straightened but not stress-relief annealed. The straightening is carried out under the conditions that; the residual stress, to which the cross-sections S_1 and S_2 are parallel and perpendicular to the rolling direction (RD) are subjected, is 50 N/mm^2 or less: and, the suspension warp of the rectangle specimens 10(1) and 10(2) is 10 mm or less.

The present invention is hereinafter explained with reference to Examples.

EXAMPLES

Al-killed steels (Nos. 1 and 2, in Table 1) and Fe-Ni based alloy (Inventive Nos. 3 – 9 and Comparative Nos. 1 –5 in Table 1) were melted. Ingots were hot-forged and hot-rolled. The oxide scale on the surface of hot-rolled sheets was removed. Cold-rolling and annealing were then repeated, and 0.12 mm thick strips were produced by the final cold-rolling. A straightening machine straightened the 0.12 mm thick strips. This machine was a tension-leveling type schematically shown in Fig. 7 and was provided with multi levelers. In the straightening, IM (inter-mesh amount of the straightening rolls) and the tension level of a strip were variously adjusted. IM at the outlet side was adjusted to such a minus side that the distance between the upper and lower rolls was equal to the sheet thickness of a strip. IM at the inlet side was adjusted to the plus side by means of changing the inclination angle between the upper and lower roll-arrays. The value of IM is shown in the ordinate of Fig. 8. The tension shown in the abscissa of Fig. 8 was controlled by means of changing the circumferential speed of bridle rolls in the inlet side.

The strip, which has passed the straightening machine, was then examined by the tensile test, the measurement of residual stress and the measurement of downward warp. In the tensile test, a JIS 13B specimen was sampled in the directions parallel and perpendicular to the rolling direction. Tensile speed was 2 mm/min.

In the measurement of residual stress, rectangle specimens 20 mm in width and 200 mm in length were etched on one of the surfaces by using the ferric chloride aqueous solution so as to warp the specimens. The radius of curvature of the specimens was measured and the residual stress was calculated. This measurement was carried out with respect to the front and back surfaces of the specimens, while changing the etching amount. Distribution of stress in the thickness direction was obtained (c.f. Hajime Sudo "Residual Strain and Distortion" published by Uchida Rokakuho Sha (1988), page 46). When the residual stress (σ) on the cross-section S_1 parallel to the rolling direction (RD) is to be measured, the rectangle specimen is sampled from a strip

elongated in the rolling direction (RD). On the other hand, when the residual stress (σ) on the cross-section S_2 perpendicular to the rolling direction (RD) is to be measured, the rectangle specimen is sampled from a strip elongated in a direction perpendicular to the rolling direction (RD). These specimens were sampled at a central portion of a strip as seen in the width direction.

Strips were cut into a form of a shadow mask 340mm in length and 270mm in width as the size of 17 in. Photo-resist was applied on both surfaces of the cut sections in the form of a shadow mask and delineated with a pattern of through holes, which was then developed. Ferric chloride solution was sprayed onto both surfaces of the cut sections to produce shadow masks. A cut section was tested as shown in Fig. 6 by the suspension method. The cut section was suspended in two directions, that is, the rolling direction of the cut section vertically or horizontally. The warp in the former direction is denoted in Table 1 as "Material, Suspension Warp, Parallel (Curl)". The warp in the latter direction is denoted in Table 1 as "Material, Suspension Warp, Perpendicular (Gutter)". When the warp was 20 mm or less, it was judged that the warp of material was acceptable. The results are shown in Table 1.

In Comparative Example 1, both curl and gutter warps of material are 10 mm or less. However, since the residual stress (σ) on the cross-section S_1 parallel to the rolling direction (RD) exceeds 50 N/mm^2, the curl warp (Wc), i.e., the warp in the direction parallel to the rolling direction (RD) of a rectangle specimen 10(1), is large.

In Comparative Example 2, both curl and gutter warps of material exceed 10 mm. In addition, the residual stress (σ) on the cross-sections S_1 and S_2 parallel and perpendicular to the rolling direction (RD) exceeds 50 N/mm^2. The gutter warp (Wg), i.e., the warp in the direction perpendicular to the rolling direction (RD) of the rectangle specimen 10(2), is large.

In Comparative Example 3, the residual stress (σ) on the cross-sections S_1 and S_2 parallel and perpendicular to the rolling direction (RD), respectively, is less than 50 N/mm^2. However, both curl and gutter warps of the material exceed 10 mm. Warp of the rectangle specimen 10(1) is, therefore, large.

In Comparative Examples 4 and 5, since the stress-relief annealing is carried out, the residual stress(a) is less than 50 N/mm^2. The warp of the rectangle specimens 10(1) and (2) is, therefore, very low. However, 0.2% YS is low as a result of the stress-relief annealing, and TS/0.2% YS > 1.03

In the inventive Examples, the post-etching shadow mask exhibits slight warp even without stress-relief annealing, and 0.2% YS is at a level close to TS.

Appropriate tension and IM conditions are dependent upon various factors.

such as rigidity of a straightening machine, lubricating condition, and thickness, shape, mechanical properties, surface roughness and residual stress of the rolled material. It is, therefore, difficult to determine the appropriate tension and IM in a manner independent of these factors. Figure. 8 illustrates, however, the tension and IM in the inventive and comparative examples. It turns out, therefore, that 10 mm or less of warp and 50 N/mm^2 or less of residual stress can be obtained in a range of from 50 to 65MPa of tension and a range of 1.2 to 1.9 mm of IM in the inventive examples.

[Table 1]

	No.	Composition (mass%)	Material							Shadow Mask		
			TS (N/mm²)	0.2%YS (N/mm²)	$\frac{TS}{0.2\%YS}$	Residual Stress (N/mm²)		Suspension Warp (mm)		Suspension Warp (mm)		Judgement
						Parallel	Perpen-dicular	Parallel (Curl)	Perpen-dicular (Gutter)	Parallel (Curl)	Perpen-dicular (Gutter)	
Example	1	Al-killed Steel	601	593	1.01	45	40	9	7	12	10	○
	2	Al-killed Steel	604	597	1.01	42	38	7	6	11	8	○
	3	Fe-36%Ni	615	610	1.01	35	20	8	7	15	8	○
	4	Fe-36%Ni	614	611	1.00	40	40	8	6	18	5	○
	5	Fe-36%Ni	629	624	1.01	20	45	7	3	3	19	○
	6	Fe-32%Ni-4%Co	665	660	1.01	43	26	8	6	11	13	○
	7	Fe-32%Ni-4%Co	658	651	1.01	38	33	7	7	7	9	○
	8	Fe-32%Ni-4%Co-0.25%Nb	685	669	1.02	36	36	6	7	16	15	○
	9	Fe-32%Ni-4%Co-0.25%Nb	694	688	1.01	41	39	4	5	6	14	○
Compa-rative Example	1	Fe-36%Ni	627	622	1.01	70	40	10	10	30	5	×
	2	Fe-36%Ni	610	602	1.01	40	80	15	18	9	32	×
	3	Fe-36%Ni	615	601	1.02	35	28	25	15	34	8	×
	4	Fe-36%Ni(Stress Relief Annealing)	590	560	1.05	10	5	3	8	4	8	○
	5	Fe-36%Ni(Stress Relief Annealing)	584	561	1.04	7	3	4	6	4	7	○